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Wave Function Effect on the Ionization Probability in the Geometrical Model

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Ionization probabilities in ion-atom collisions at zero impact parameter have been calculated in the geometrical model using the Hartree-Fock-Roothaan wave functions. The obtained results for various atomic shells are shown graphically and compared with those from the hydrogenic wave functions. The wave function effect on ionization probabilities is discussed.

KEY WORDS: Ionization probability/ Geometrical model/ Hartree-Fock-Roothaan wave functions/

1. INTRODUCTION

In inner-shell ionization processes of atoms by heavy-ion impact, it is well known that simultaneous transitions of more-than-one electrons are important because of strong perturbation caused by the projectile nuclear charge. Among multi-electron transitions, the multiple ionization process has been extensively studied both experimentally and theoretically.¹⁾ Except for the case of simultaneous electron ejection from the same atomic subshell, the electron correlation effect is not important and the multiple ionization process can be treated within the framework of the independent electron model.²⁾ In this model the probability distribution of the multiple ionization at the fixed impact parameter is expressed by the binomial distribution constructed from the ionization probability for each electron.

Using the semiclassical approximation (SCA), Hansteen and Mosebekk³⁾ calculated the K- and L-shell ionization probabilities for protons on Cu as a function of impact parameter and obtained the KLⁿ multiple vacancy distributions by integrating the binomial distribution over impact parameter. In the case of multiple ionization involving the inner-shell vacancy, we may replace the ionization probability per *i*-shell electron at the impact parameter *b*, $p_i(b)$, by an average value $p_i \simeq p_i(0)$, because $p_i(b)$ for the inner-shell electron falls off rapidly with increasing *b*.

Hansen⁴⁾ and McGuire and Richard⁵⁾ estimated p_i by the binary-encounter approximation (BEA). However, according to the SCA and the BEA, the ionization probability is proportional to Z_1^2 , where Z_1 is the projectile charge. This fact means that for highly-charged projectiles the ionization probability exceeds unity and violates the unitarity condition.

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On the other hand, Becker *et al.*⁶⁾ performed coupled-channel calculations for multiple L-shell vacancy production in coincidence with K-shell vacancy in the independent Fermi particle model. Their results show the saturation effect of $p_L(0)$ with Z_1 at the fixed impact velocity. However, the calculations are complicated and it is difficult to extend their model to outer-shell multiple ionization.

Recently, Sulik *et al.*⁷⁾ developed the geometrical model to calculate $p_i(0)$ at high-velocity limit in the BEA of Thomson.⁸⁾ The ionization probability obtained in this model has simple scaling rule as a function of Z_1/v_1 , where v_1 is the projectile velocity. It also shows the unitarity for increasing Z_1 and is universal for the target atomic number Z_2 . Sulik and Hock⁹⁾ improved their model for low-velocity region of the projectile. The geometrical model has been successfully used to interpret the experimental data of ionization probabilities at zero impact parameter^{10,11)} and is in reasonably agreement with the results of coupled-channel calculations of Becker *et al.*¹²⁾

The geometrical model is very useful to estimate the production of multiple vacancies in ion-atom collisions because of its simplicity and its possibility for application to outer-shell electrons. However, up to now all the calculations have been made for hydrogenic wave functions. In the case of outer-shell ionization, the screening effect due to the presence of other atomic electrons may cause the change in shape of wave functions and thus ionization probability. It is the purpose of the present work to calculate ionization probability at zero impact parameter in the geometrical model using more realistic atomic wave functions than the hydrogenic ones and to test the wave function effect on the ionization probability. For this purpose, we use the Hartree-Fock-Roothaan (HFR) method to calculate the atomic wave functions because the HFR wave functions are given in terms of simple basis functions and all the calculations can be made analytically.

2. THEORETICAL

According to the geometrical model,⁷⁾ the ionization probability of the target electron with the principal quantum number n and the orbital angular momentum quantum number l for the projectile with zero impact parameter with respect to the target nucleus is given by

$$p_{nl}(b_e) = 1 - \int_{b_e}^{\infty} dr r^2 R_{nl}^2(r) \left[1 - \left(\frac{b_e}{r} \right)^2 \right]^{1/2}. \quad (1)$$

where $R_{nl}(r)$ is the radial part of the electron wave function and b_e is the impact parameter with respect to the target electron. Throughout the present work, atomic units ($e=m_e=\hbar=1$) are used.

The quantity b_e is a function of energy transfer in Rutherford scattering, but in the high-velocity limit we can use

$$b_e = \frac{2Z_1 n}{Z_2 v_1}. \quad (2)$$

For low and medium velocity region, the value of b_e can be chosen so that the ionization cross section by the Thomson's BEA,⁹⁾ on which the geometrical model is based becomes equal to that by the modern BEA.¹³⁾ In this case, b_e is expressed as⁹⁾

$$b_e = \frac{Z_1}{v_1} V \left[\frac{2G(V)}{I_{n1}} \right]^{1/2}, \quad (3)$$

where $V=v_1/v_2$ is the scaled projectile velocity, v_2 is the velocity of the target electron, I_{n1} is the ionization potential of the atomic electron, and $G(V)$ is the BEA scaling function.⁵⁾

Substituting b_e into Eq. (1) and changing the variable from r to $t=a_n r$, where a_n is twice of the reciprocal of the Bohr radius corresponding to the principal quantum number n and the atomic number Z_2 , the ionization probability can be written by

$$p_{n1}(x) = 1 - \frac{1}{a_n^3} \int_x^\infty dt t R_{n1}^2(t) (t^2 - x^2)^{1/2}. \quad (4)$$

Here the parameter $x=a_n b_e$ is obtained from Eq. (3) as

$$x = 4 \frac{Z_1}{v_1} V [G(V)]^{1/2}. \quad (5)$$

For hydrogenic wave functions,¹⁴⁾ the general form of the integral in Eq. (4) can be expressed as

$$\begin{aligned} I_m(x) &= \int_x^\infty dt t^m e^{-t} (t^2 - x^2)^{1/2} \\ &= J_m(1, x) \\ &= \left[\left(-\frac{\partial}{\partial \mu} \right)^m J_0(\mu, x) \right]_{\mu=1}, \end{aligned} \quad (6)$$

where

$$J_m(\mu, x) = \int_x^\infty dt t^m e^{-\mu t} (t^2 - x^2)^{1/2}. \quad (7)$$

According to Gradshteyn and Ryzhik,¹⁵⁾

$$\int_x^\infty dt t^{-\mu} (t^2 - x^2)^{\nu-1} = \frac{\Gamma(\nu)}{\pi^{1/2}} \left(\frac{2x}{\mu} \right)^{\nu-1/2} K_{\nu-1/2}(\mu x),$$

where $\Gamma(x)$ is the gamma function and $K_\nu(x)$ is the modified Bessel function of the 2nd kind with order ν . For $\nu=3/2$, Eq. (7) with $m=0$ is expressed as

$$J_0(\mu, x) = \frac{x}{\mu} K_1(\mu x). \quad (8)$$

From Eq. (8) and the recurrence formula of $K_\nu(x)$,¹⁶⁾ we obtain

$$J_1(\mu, x) = \frac{2x}{\mu^2} K_1(\mu x) + \frac{x^2}{\mu} K_0(\mu x), \quad (9)$$

and

$$J_2(\mu, x) = \left(\frac{6x}{\mu^3} + \frac{x^3}{\mu} \right) K_1(\mu x) + \frac{3x^2}{\mu^2} K_0(\mu x). \quad (10)$$

The integral for $m \geq 3$ can be calculated from the recurrence formula

$$J_m = \frac{m+1}{\mu} J_{m-1} + x^2 J_{m-2} - \frac{m-2}{\mu} x^2 J_{m-3}. \quad (11)$$

Here we use the abbreviation J_m for $J_m(\mu, x)$.

From Eqs. (6)~(11), the ionization probability for an arbitrary shell can be obtained analytically as a function of the parameter x . The explicit results for nl shells up to $n=4$ are listed in Ref. 10.

In the case of the HFR model, the radial wave functions are expanded in terms of the Slater-type orbitals (STO's):

$$R_{nl}(r) = \sum_i c_i N_i r^{n_i-1} \exp(-\zeta_i r), \quad (12)$$

where c_i is the expansion coefficient, n_i is the principal quantum number, ζ_i is the orbital exponent of the STO, and

$$N_i = \left[\frac{(2\zeta_i)^{2n_i+1}}{(2n_i)!} \right]^{1/2}.$$

The values of c_i , n_i , and ζ_i for each element are tabulated by Clementi and Roetti¹⁷⁾ for $2 \leq Z_2 \leq 54$ and by McLean and McLean¹⁸⁾ for $55 \leq Z_2 \leq 92$.

Substituting Eq. (12) into Eq. (4), the ionization probability is written as

$$p_{nl}(x) = 1 - \sum_{ij} \frac{1}{a^{n_i+n_j+1}} c_i c_j N_i N_j I\left(n_i+n_j, \frac{\zeta_i+\zeta_j}{a_n}, x\right) \quad (13)$$

where

$$\begin{aligned} I(n, \zeta, x) &= \int_x^\infty dt t^{n-1} e^{-\zeta t} (t^2 - x^2)^{1/2} \\ &= J_{n-1}(\zeta, x). \end{aligned} \quad (14)$$

It should be noted that for the hydrogenic model, the ionization probability is universal for Z_2 . On the other hand, Eq. (13) in the HFR model depends on Z_2 . In this case, the atomic charge Z_2 in the parameter a_n and x should be replaced by an appropriate value. For this purpose, we introduce the screening constant σ and use the effective nuclear charge $Z_{\text{eff}} = Z_2 - \sigma$ instead of Z_2 . The screening constant is calculated with the HFR wave function by¹⁹⁾

$$\sigma = Z_2 - \langle r_H \rangle / \langle r \rangle, \quad (15)$$

where $\langle r_H \rangle$ is the mean radial distance for the hydrogenic wave function, $\frac{1}{2}[3n^2 - l(l+1)]$, and $\langle r \rangle$ is that for the HFR wave function.

However, it is well known that this screening constant is good for wave functions, but poor for ionization potentials in Eq. (3). To improve the approximation for

ionization potential, we introduce another screening parameter for energies as a ratio of the realistic ionization potential to the ideal one for Z_{eff} , $\theta_{nl}=2E_{nl}/(n^2Z_{\text{eff}}^2)$, where E_{nl} is the energy eigenvalue in the HFR model. The parameter x in the present model can be expressed as

$$x = 4 \frac{Z_1}{v_1} \left[\frac{G(V)}{\theta_{nl}} \right]^{1/2}. \quad (16)$$

3. RESULTS AND DISCUSSION

The ionization probabilities per electron at zero impact parameter have been calculated in the geometrical model with the HFR-type wave functions as a function of a universal parameter x . The obtained results are shown graphically in Figs. 1–9 and compared with the values by the hydrogenic wave functions. For K, L, and M shells, the results with $Z_2=29, 47$, and 79 are shown, while those with $Z_2=79, 83$, and 92 are presented for N subshells.

It is clear that all the curves increase with increasing x and approach to unity, i.e. the unitarity condition is fulfilled. Although the ionization probability with the HFR wave functions depends on Z_2 , its behavior as a function of x is almost same for all elements and close to that with the hydrogenic wave functions. It is quite natural because the ionization probability in the hydrogenic model is universal for Z_2 and thus $p_{nl}(x)$ in Eq. (4) can be considered as the value for the screened hydrogenic model with Z_{eff} . This result seems to indicate an approximate universal property of $p_{nl}(x)$ for Z_2 , but it should be noted that the parameter x in the HFR model includes the screening parameter θ_{nl} and depends on Z_2 .

For K shell, the wave function effect is small and all the HFR results are in agreement with the hydrogenic value. The wave function effect becomes larger for outer-shell electrons. This is because in outer shells the screening effect from many inner-shell electrons is complicated and the wave function cannot be represented as a simple hydrogenic shape.

The HFR values in general oscillate around the hydrogenic ones for small x and the difference between them becomes larger for smaller Z_2 . This fact can be explained as follow. At small distance, i.e. near the nucleus, the perturbation effect due to the presence of other atomic electrons is large and the deviation of the shape of the HFR wave function from that of the hydrogenic one is large. As can be seen from Eqs. (4) and (14), for small x the contributions from the region with small radial distance are important. When the number of electrons is small, the small perturbation caused by the screening effect due to other electrons leads to a large relative change in the shape of atomic wave functions and the wave function effect is larger for smaller Z_2 .

In order to demonstrate the wave function effect, the relative ratios of the ionization probability obtained with the HFR wave function to that with the hydrogenic wave function are shown in Figs. 10–15. It can be seen that in all cases the HFR values oscillate around the hydrogenic curves. The oscillation is larger for small x and for smaller Z_2 values, as has been discussed above. When the wave

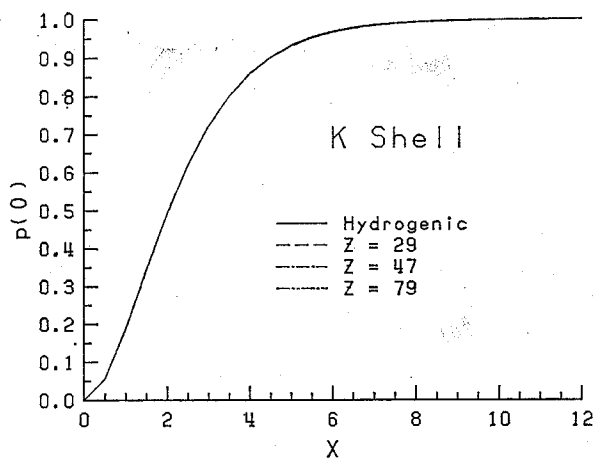


Fig. 1. The ionization probabilities per electron for K shell at zero impact parameter as a function of the parameter x . The solid curve represents the result with the hydrogenic wave function, the dashed curve with the Hartree-Fock-Roothaan wave function for copper, the dot-dashed curve for silver, and the double-dot-dashed curve for gold.

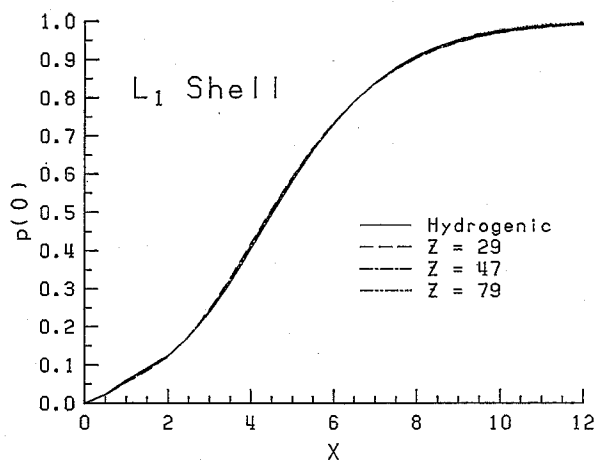


Fig. 2. The same as Fig. 1, but for L₁ shell.

Wave Function Effect on the Ionization Probability

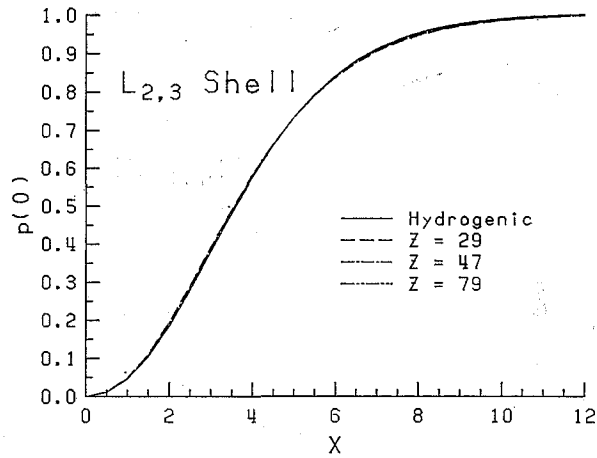


Fig. 3. The same as Fig. 1, but for $L_{2,3}$ shell.

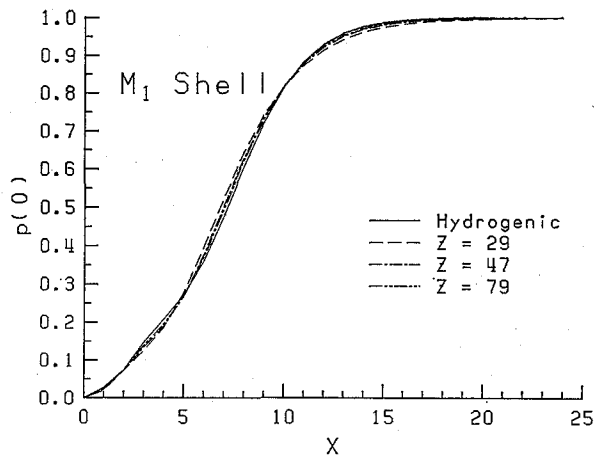


Fig. 4. The same as Fig. 1, but for M_1 shell.

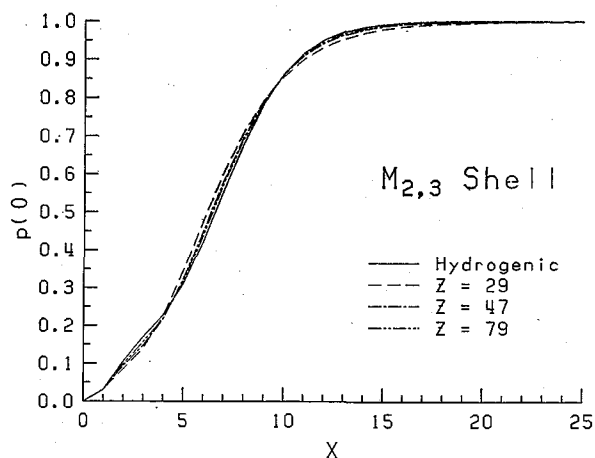


Fig. 5. The same as Fig. 1, but for M_{2,3} shell.

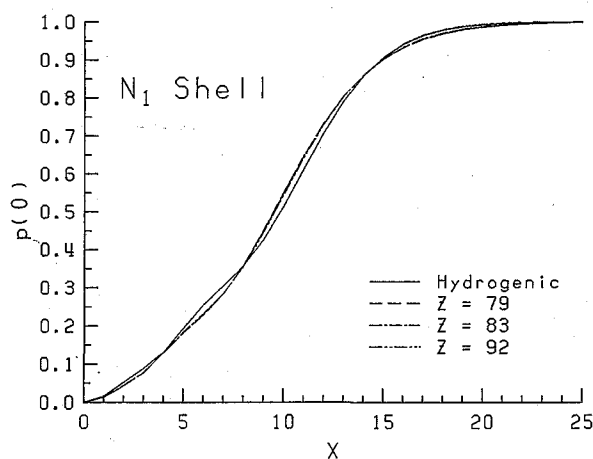


Fig. 6. The ionization probabilities per electron for N₁ shell at zero impact parameter as a function of the parameter x . The solid curve represents the result with the hydrogenic wave function, the dashed curve with the Hartree-Fock-Roothaan wave function for gold, the dot-dashed curve for bismuth, and the double-dot-dashed curve for uranium.

Wave Function Effect on the Ionization Probability

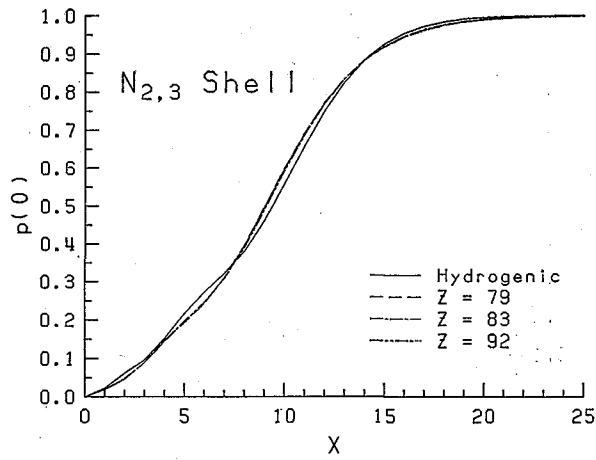


Fig. 7. The same as Fig. 6, but for $N_{2,3}$ shell.

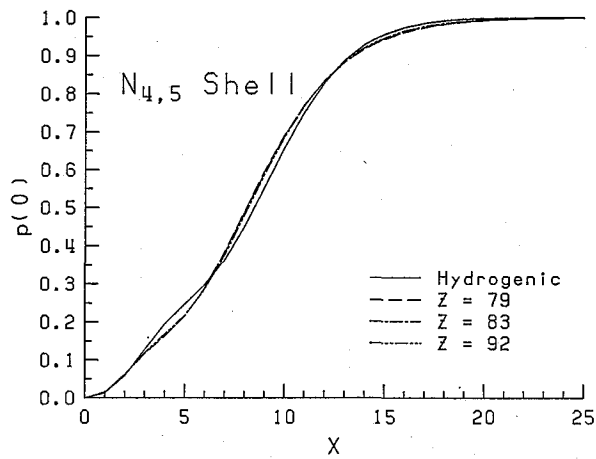


Fig. 8. The same as Fig. 6, but for $N_{4,5}$ shell.

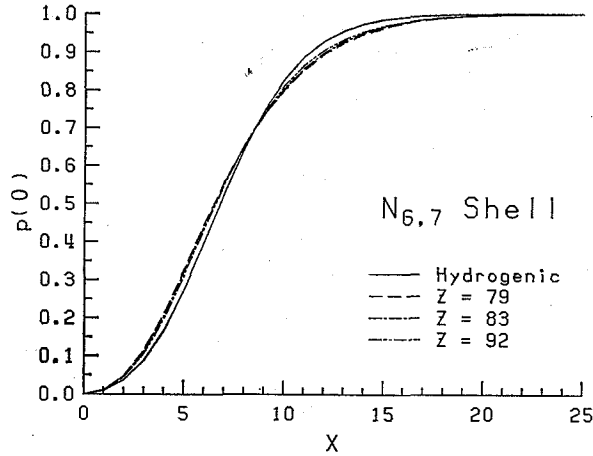


Fig. 9. The same as Fig. 6, but for $N_{6,7}$ shell.

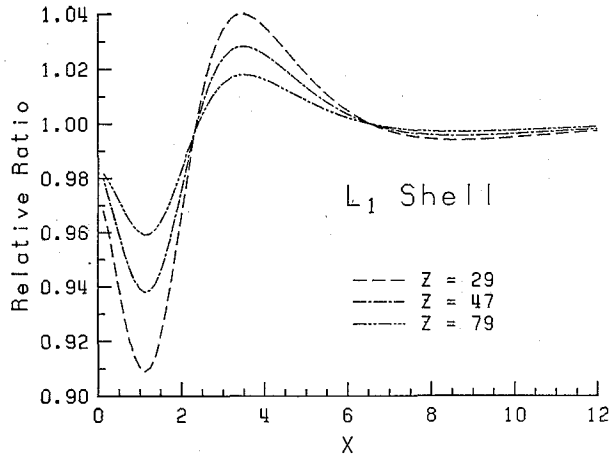


Fig. 10. Relative ratio of the ionization probability for L_1 shell calculated with the Hartree-Fock-Roothaan wave function to that with the hydrogenic one. The dashed curve represents the ratio for copper, the dot-dashed curve for silver, and the double-dot-dashed curve for gold.

Wave Function Effect on the Ionization Probability

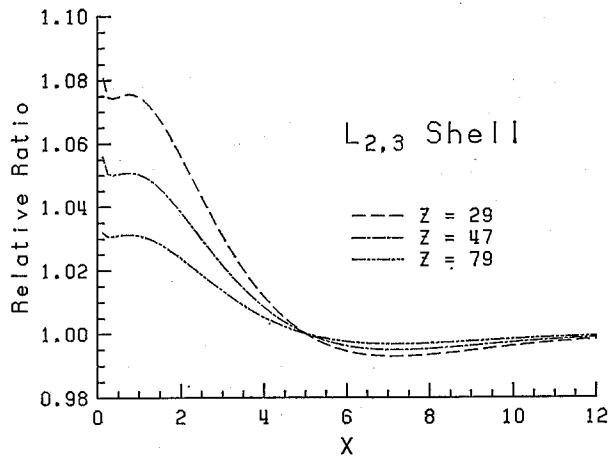


Fig. 11. The same as Fig. 10, but for $L_{2,3}$ shell.

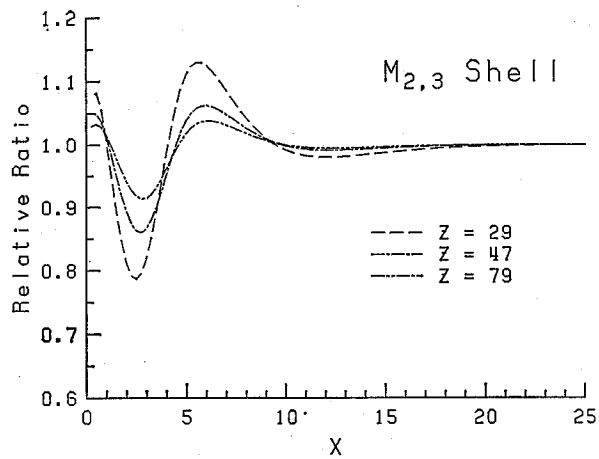


Fig. 12. The same as Fig. 10, but for $M_{2,3}$ shell.

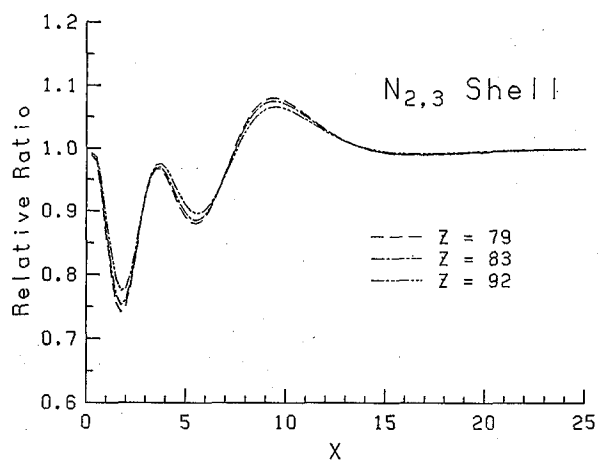


Fig. 13. Relative ratio of the ionization probability for $N_{2,3}$ shell calculated with the Hartree-Fock-Roothaan wave function to that with the hydrogenic one. The dashed curve represents the ratio for gold, the dot-dashed curve for bismuth, and the double-dot-dashed curve for uranium.

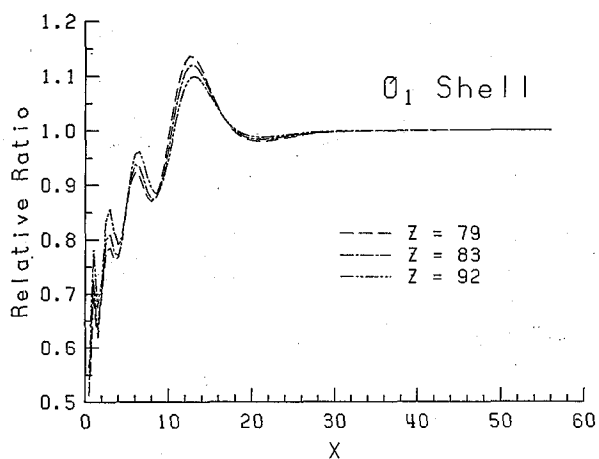


Fig. 14. The same as Fig. 13, but for O_1 shell.

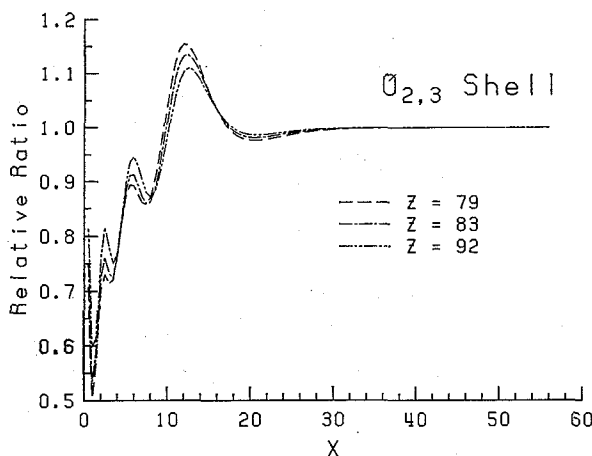


Fig. 15. The same as Fig. 13, but for $O_{2,3}$ shell.

function has nodes, for example in L_1 , $M_{2,3}$, and $N_{2,3}$ shells, the ratio as a function of x has a structure, i.e. there are bumps. These bumps are attributed to the difference in the positions of nodes between the HFR and hydrogenic wave functions. Therefore, the number of bumps corresponds to the number of nodes of the wave function.

In conclusion, we have calculated the ionization probabilities at zero impact parameter in the geometrical model using the HFR wave functions. The ionization probability shows an approximate scaling property for Z_2 as a function of the universal parameter x . However, it should be noted that in the present model the parameter x itself is a function of Z_2 . The HFR values oscillate around the hydrogenic ones because of the difference in the screening effect due to other atomic electrons. This wave function effect is larger for smaller target atomic numbers and for outer-shell electrons, i.e. for larger principal quantum numbers.

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